Characterizing Fluorotelomer and Polyfluoroalkyl Substances in New and Aged Fluorotelomer-Based Polymers for Degradation Studies with GC/MS and LC/MS/MS

John W. Washington,*,[†] Jonathan E. Naile,[†] Thomas M. Jenkins,[‡] and David G. Lynch[§]

[†]National Exposure Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia 30605, United States
[‡]Senior Environmental Employment Program, U.S. Environmental Protection Agency, Athens, Georgia 30605, United States
[§]Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, Washington, DC 20460, Untied States

* Supporting Information
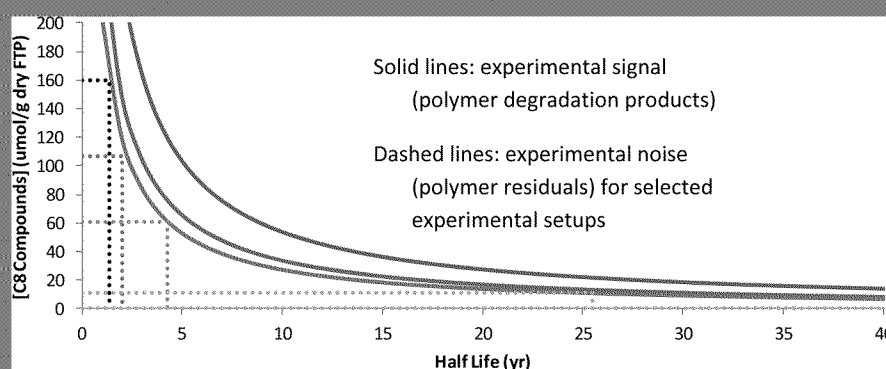
Fluorotelomer-based polymers (FTPs), the dominant product of the fluorotelomer industry, are antistaining and antiwetting agents that permeate the products and surfaces of modern society. However, the degree to which these materials expose humans and the environment to fluorotelomer and perfluorinated compounds, including recalcitrant and toxic compounds such as perfluorooctanoic acid (PFOA), is ill-defined. The design intent of FTPs, to minimize interaction with other substances, including solvents, heretofore has stymied efforts to develop robust methods to characterize the content of monomers and associated compounds of new commercial FTPs, as well as commercial FTPs that have been aged in environmental media for degradation testing. Here we show that FTPs can be exhausted of these compounds and quantitated by (i) drying the FTP on a suitable substrate at elevated temperature to achieve low, constant monomer concentrations; (ii) serial extraction with MTBE for fluorotelomer-monomer analysis by GC/MS in PCI mode; followed by (iii) serial extraction with 90/10 ACN/H_2O for polyfluorocompound analysis by LC/MS/MS in negative ESI mode. This approach yields exhaustive, internally consistent accounting of monomers and associated compounds for FTPs, either alone or in a soil matrix (representing an environmental medium), for both new and simulated-aged FTPs to allow degradation testing, and for fluorinated compounds at least as long as C12.

■ INTRODUCTION

Fluorotelomer substances (FTSs) are marvels of modern society. Imparting antiwetting and antistaining properties to consumer products including clothing, upholstery, carpeting, painted surfaces, food containers, cookware, and more, FTSs invisibly shield the surfaces of our daily lives, vastly easing the burden of countless cleaning and maintenance tasks. But this convenience comes at a cost. Long-standing concerns associated with the fluorotelomer industry center on FTSs and FTS degradation products (hereafter grouped as poly- and perfluoroalkylate substances; PFASs), notably including perfluorooctanoic acid (PFOA). Some of these PFASs have been shown to be persistent in the environment,[1−3] widely detectable in the general human population,[4] and toxic to humans[5] and other animals.[6,7]

Among the variety of commercial FTSs, side-chain-fluorinated polymers (or fluorotelomer-based polymers; FTPs) comprise the largest part; about 80% of all FTSs manufactured and used worldwide are FTPs.[8] Because FTPs permeate modern society, they potentially constitute a central component for exposure of the general population to FTSs and associated PFASs. Moreover, the best existing evidence indicates that at least some FTPs degrade under the environmental conditions that can be expected upon landfill disposal, forming FTSs and PFASs.[9,10] With the elucidation of

these conspiring factors, the EPA promulgated requirements for testing proposed new FTPs before market introduction to determine whether the product presents an unreasonable risk,[11] and the EPA and major fluorotelomer manufacturers agreed that the prudent course was to cease production of long-chain FTSs by 2014.[12] To accommodate this agreement, industry is developing FTPs using shorter-chained telomers right now.[13] Consequently, there is a pressing need to characterize the species and concentrations of FTSs and PFASs in existing FTPs, and this need will persist in the future as new short-chained FTPs, having unknown residuals and susceptibilities to environmental degradation, enter the market. However, because the requirements to test new FTPs were promulgated recently, there is no established protocol for this testing.

Unfortunately, the very traits that make FTPs so useful also render them uniquely challenging and confounding to characterize analytically. Specifically, FTPs and PFASs

   (i) bear a F-saturated telomer designed to repel all nonfluorinated materials;

   (ii) have terminal moieties intended to bind tightly with other molecules or surfaces; and

   (iii) share a propensity to remain coassociated with other fluorinated molecules when in the presence of a nonfluorinated matrix, a phenomenon often termed "fluorophilicity".

Together, these traits challenge dissolution of the intended analytes during extraction and render the extracted compounds susceptible to loss during handling and analysis. Compounding these challenges, every FTP is unique in terms of structure, consequently the efficacy of extraction and analysis methods varies drastically among FTPs.

Degradation testing adds still more complexity to the basic objective of characterizing residual content of a new FTP in that extraction and analysis ideally will be equally efficacious in quantitating the complete reservoir of all analytes whether (i) the FTP stands alone in the extraction vessel or is in the presence of an environmental medium that supports a microbial consortium, e.g., soil or sewage media; and (ii) whether the FTP is new or aged for stability testing.

Here we report on variables and challenges in developing methods to characterize the residual/impurity content of existing and future FTPs, and to evaluate their degradability in environmental media, as well as testing methods we developed to be robust in the context of these challenges.

BACKGROUND

FTP Structure. The structural basis of FTPs is a carbon backbone to which fluorotelomers and nonfluorinated moieties are appended (Figure 1). The fluorotelomers are composed of $-CF_2-$ groups in which the fluorine is covalently bound. Given that fluorine is the most electronegative element, covalent completion of its valence shell effectively yields the electronic structure of a substrate-bound Ne noble gas, thereby conferring remarkably low reactivity. Most fluorotelomers are synthesized by the telomerization process wherein units of tetrafluoroethylene taxogens are bound to the chain terminus (Supporting Information (SI) Figure S1). Consequently, FTPs are comprised solely with even-numbered fluorotelomers, generally ranging in perfluorinated carbons from C4 to C20, the specific proportions of which are patented, proprietary information determined to be well suited to the FTP's intended purpose. The terminal groups, through which the fluorotelomer chains
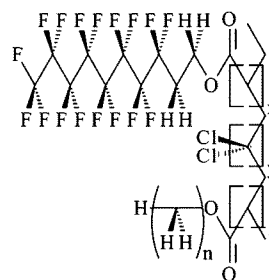

Figure 1. General structure of an FTP after Russell et al.[15] A carbon backbone bears (1) fluorinated telomers, which act as repellents to soiling and wetting agents; and (2) nonfluorinated moieties that anchor the FTP to the intended substrates by van der Waals and/or hydrogen bonding. Depicted here with $(CF_2)_2 = 4$, the fluorinated telomers generally range from $(CF_2)_2 = 3-10$, including the chain terminus.

are bound to the carbon backbone, usually are a carboxylate, sulfonate, phosphate ester, carbamate, or similar.

Because FTPs are composed of a mélange of monomers, they do not possess a unique stoichiometry or structure. For this reason, other than early research using matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF),[14] FTPs are not characterized by direct analysis. Instead characterization efforts concentrate on analysis of the FTS monomers and PFASs that remain in the FTP as residuals from synthesis or impurities in the stocks (SI Figure S1).[10] Experiments intended to determine whether and how fast an FTP might degrade, usually do so by comparing molar sums of the PFASs in aged FTPs (SI Figure S1) versus that of the new raw product; in the absence of direct analysis of FTPs, degradation is inferred from increases of degradation products during FTP-aging studies.

FTP Sols. When FTPs are delivered to manufacturers for incorporation into consumer products, commonly the FTPs are delivered as aqueous sols, with the ~100−300 nm (nominal diameter)[15] FTP particles suspended in the bulk phase. Being denser than water[10] and hydrophobic, the FTPs will remain in suspension only with considerable modification of the liquid phase with surfactants to decrease the interfacial tension between FTP surfaces and the solvent. A large fraction of these surfactants are fluorotelomer monomers. Within the context of regulatory allowance, fluorotelomer-monomer concentrations can range as high as 2 wt % of the dry FTP.[16]

The physical state of these FTP sols presents challenges for FTP characterization and degradation testing, e.g., (i) the sols are metastable and small changes in composition as part of sample preparation can result in precipitation of the FTP; and (ii) the high initial fluorotelomer-monomer concentrations of FTP sols, along with attendant analytical uncertainty, potentially can mask FTP degradation in all but very short-lived FTPs, i.e., at high initial monomer concentrations, analytical uncertainty might exceed monomer/PFAS ingrowth from degradation during testing.

Residuals and Impurities. For FTPs and FTP sols, residuals are the monomers used to synthesize the FTP that remain unpolymerized in the final commercial product. For an acrylate-linked FTP (Figure 1), residuals often include fluorotelomer acrylate (FTAc) and alcohol (FTOH) monomers (SI Figure S1). In contrast, impurities in FTPs and FTP sols are PFASs present in FTPs and sols that were not intended, neither in the FTP nor the feed stocks, e.g., fluorotelomer acids and perfluorocarboxylates (PFCAs; SI
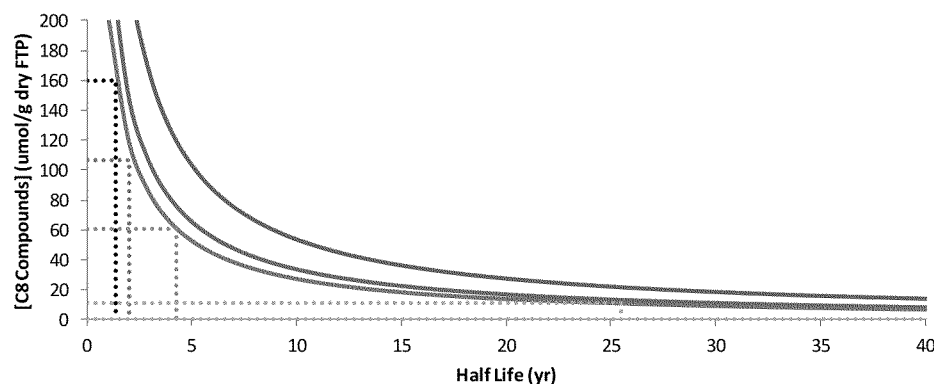
Figure 2. Residual 8-2FTOH for selected treatments of FTP4 compared to expected FTP degradation-product concentration for a one-year experiment as a function of modeled FTP4 half-life. Solid lines are modeled degradation-product concentrations as a function of half-life: products generated (blue), products recovered by extraction (pink), and typical 2 standard deviation uncertainty among reps (yellow). Dashed lines are residual 8-2FTOH concentrations for commercial sol (equating to half-life of 1.4 y), purified raws sol (2.0 y), 21 °C dried (4.3 y), 50 °C dried (25 y), and 127 °C (≥ 200 y). See SI Discussion S2 for complete explanation.

Figure S1). In our experience,[10] in new FTPs, residuals commonly are present on the order of >100× that of impurities, with residuals being present in the parts-per-thousand to percent range and impurities commonly in the low parts-per-million range (SI Table S1).[10] When FTPs are aged under real or simulated environmental conditions, e.g., FTP–soil microcosms in laboratory settings to simulate landfill settings, the residuals present in the initial FTP biodegrade so that impurities can accumulate to high concentrations under environmental conditions.[10,17,18]

In past efforts, residuals have been extracted from FTPs by tetrahydrofuran (THF)[19] and methyl tert-butyl ether (MTBE) in the presence of H_2O.[10] Often bearing an electrostatic charge, impurities have been extracted from FTPs with "Fluorocarbon 113"[19] or acetonitrile (ACN)–H_2O solutions.[10]

METHOD DEVELOPMENT

Here we report method-development efforts and results together so that the contextual logic for proceeding from one effort to another is clear to the reader. All research reported herein used commercial FTP sols prepared by DuPont Corporation and delivered to EPA as part of a Supplemental Environmental Project.[20] Analytical methods employed in this study are similar to those we reported in detail earlier (SI);[3,17] gas chromatograph/mass spectrometer (GC/MS) parameters are summarized in SI Table S2, and liquid chromatograph/tandem mass spectrometer (LC/MS/MS) parameters are in SI Table S3. Quantitations were performed with mass-labeled internal standards added to all standards and samples unless stated otherwise (SI).

Typical Analytical Difficulties with FTPs and FTP Sols. Fluorotelomer and perfluorinated compounds are notoriously challenging analytes, both in terms of extractability and handling,[21,22] as well as due to their presence at trace levels in components of analytical instruments sometimes necessitating instrument modifications to achieve lower detection limits.[23] But even within this context, fluorotelomer polymers stand out in terms of presenting unique challenges to dependable quantification. We summarize some of these challenges in the SI (Discussion S1).

Residuals vs Form and Handling of FTP. Studies on the stability/degradability of FTPs generally are carried out by monitoring increases in the sum of fluorotelomer and perfluoro analytes in FTP–soil microcosms over months of incubation.

Given that each analysis has an attendant analytical uncertainty, that replicate microcosms vary among each other, and that FTP half-lives are long relative to the practical length of most experiments, the high levels of residuals in FTP sols (SI Table S1) potentially can obfuscate evidence of degradation. This quandary is illustrated in Figure 2 which compares residual FTOH concentrations of selected FTP preparations to degradation-product concentrations expected for a range of FTP half-lives following a one-year FTP incubation; for most FTP preparations, in all but the shortest half-lives, the noise from residual FTOH equals or exceeds the signal of the degradation products. For this reason, in FTP-degradation studies, minimization of initial residuals is highly desirable. Here we examine the efficacy of various efforts to minimize residuals in FTPs.

Residuals vs FTP Synthesis Details. An inventive early effort at minimizing residuals in FTP sols entailed sparging with inert gas.[24] Following this lead, in an effort to minimize residuals, DuPont synthesized test versions of their commercial FTP sols by four methods:[20] (i) conventional commercial preparation; (ii) bench preparation using commercial reagents; (iii) bench preparation with purified reagents; and (iv) sparging of a commercial sol. In Figure 3, we depict dominant residuals for two of these DuPont/EPA FTP sols, identified herein as FTP3 and FTP4, prepared by each of the four methods. For these commercial FTP sols, bench synthesis with purified reagents generally fell at or near the lowest residuals; however, even this most effective preparation yielded a sol having roughly 70–80% of the residual FTOHs present in the commercial FTP4 formulation for example (Figure 3). Sparging tended to generate the next lowest levels of residuals; unsurprisingly, however, fluorotelomer iodides exhibited little to no measurable effect from sparging (Figure 3). These results suggest that the residual content of at least some commercial FTP sols cannot be dramatically affected by preparation or handling of the sol itself. And in terms of a starting point for FTP degradation testing, these alternative preparation techniques offer little advantage (Figure 2, SI Discussion S2).

Residuals vs Time and Pressure during Air Drying. Given the modest reduction in residuals achieved with manipulation of commercial FTP sols, and the ancillary fact that consumers usually are exposed only to applied/dried FTPs, we investigated the effect of drying FTP sols on the residuals. We first tried air drying FTP4 for 4 days. Observing roughly constant mass from
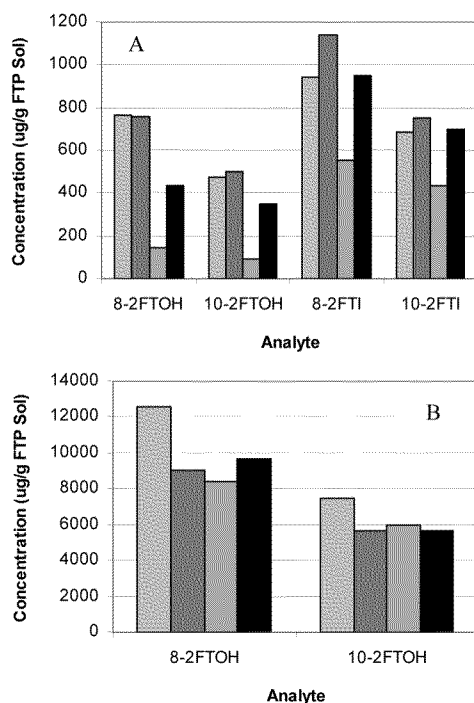
Figure 3. Fluorotelomer alcohol (FTOH) and iodide (FTI) monomers for FTP3 (a) and FTP4 (b) sols, prepared by four methods, as determined by dissolution in MTBE and GC/MS analysis: commercial product (blue), bench-synthesized with commercial raw materials (red), bench-synthesized with purified raw materials (yellow), gas-sparged commercial product (black).

10 h on, suggesting drying largely was complete, we then measured residuals in the air-dried FTP four times over the course of a month (SI Figure S8). These efforts documented an evaporative loss of FTOH residuals of ~40–50% relative to the original FTP sol (SI Discussion S2). However (1) it was unclear whether the FTOHs had attained steady-state concentration long after mass had stabilized (SI Figure S8); and (2) this residual reduction offers little benefit in terms of detecting FTP degradation (Figures 2 and SI S7).

In a parallel effort, we investigated FTP4 residual concentrations with drying under vacuum in a desiccator at room temperature. Resulting FTOH concentrations exceeded those achieved in the open lab setting, probably at least partially owing to less air circulation and FTOH accumulation in the desiccator head space.

Residuals vs Temperature during Drying. Application of FTPs to consumer products often entails a heating step. For example, a patent describing the structure and performance of an acrylate-linked FTP, that is identical to our test FTP4 to our degree of knowledge, was applied to paper substrate at 127 °C.[25] Following this practice, we investigated FTOH residuals as a function of drying temperature (SI Figure S9). So that residual monomers did not accumulate in the oven headspace during drying, thereby impeding further volatilization, we circulated lab air through the oven during drying (SI Figure S10). Heating yielded dramatic decreases in FTOH residuals, the relationship approximating a vant'Hoff-type function (SI Figure S9b). The FTP dried at 127 °C retained FTOHs at levels roughly 500× lower than in the original FTP sol, on a per-mass dry FTP basis, a decrease that should greatly enhance the potential to detect FTP degradation-product ingrowth (Figure 2; SI Discussion S2).

Residuals vs Time during 127 °C Drying. The patent describing drying at 127 °C reported the drying time as 2 min, a period compatible with commercial-scale processing. For the purpose of testing FTPs, however, one needs to minimize variation among replicates in residual monomer content, as well as ensure that the heat treatment does not degrade the FTP. Our strategy for assuring reproducibility among microcosms entailed determining the shortest heating time required to obtain quasi-steady-state concentrations of the dominant residuals. Figure 4 depicts several residual concentrations
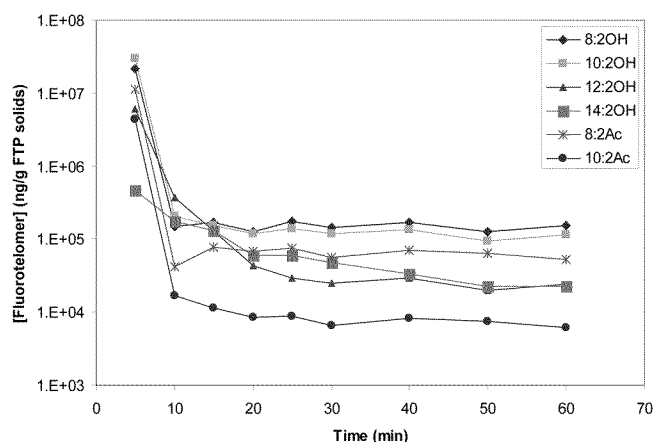

Figure 4. Geometric mean monomer concentration (n = 3) for samples heat cured at 127 °C, taken at 5- and 10-min intervals for 1 h. Data are for 3 serial MTBE extractions that were composited and analyzed. Similar drying tests, but for longer periods, are depicted in SI Figure S11 to document continued stability in monomer concentrations with protracted heating.

through time while drying the test FTP at 127 °C. To evaluate whether protracted heating at 127 °C induced FTP degradation, we also checked residual concentrations over a several-day heating period (SI Figure S11), reasoning that FTP degradation would be reflected in increases of monomer and/or residual-type species. Seeing no considerable monomer or residual increases with protracted heating (SI Figure S11), we inferred heating the test FTP at 127 °C did not measurably damage the FTP. Based on the data in Figure 4, we settled on 20 min as a suitable 127 °C drying period for our test FTP.

Exhausting Fluorotelomer Residuals through Serial Extractions. Two solvents have been shown to disperse FTPs into the bulk liquid phase effectively: THF[19] and MTBE.[10] The low surface tension between these solvents and FTPs also renders these solvents effective in dissolving fluorotelomer monomers in the presence of new FTPs.[10,19]

For the objective of testing the stability of FTPs under environmental conditions (e.g., disposal in a landfill), the chosen fluorotelomer-extraction solvent also must remain effective in environmental matrices, which generally include natural organic matter (NOM), microbes, and microbial enzymes. To assess the efficacy of serial MTBE extractions for exhausting fluorotelomer monomers from FTPs and FTP–soil microcosms, we prepared the FTP by air drying it on a cotton tuft for 118 h. In triplicate centrifuge tubes, we extracted FTP-impregnated cotton by itself and in the presence of ~5 g of soil. The soil and FTP-impregnated cotton tufts were mixed by saturating the entire mass and vortexing until contact appeared intimate. Intended to be the design for future degradation experiments, these experimental units were called

microcosms. For the extraction process, we employed an approach similar to that of Ellington et al.[26] in that bulk phases of MTBE and water both were present, and the extraction tubes were rotated on a rotisserie overnight. After each overnight rotation, MTBE was removed from the tube, another MTBE aliquot was added, and the extraction was repeated for a total of eight extraction steps. Results of this effort are depicted in Figure 5a and b; whether in the presence of soil or not, for both
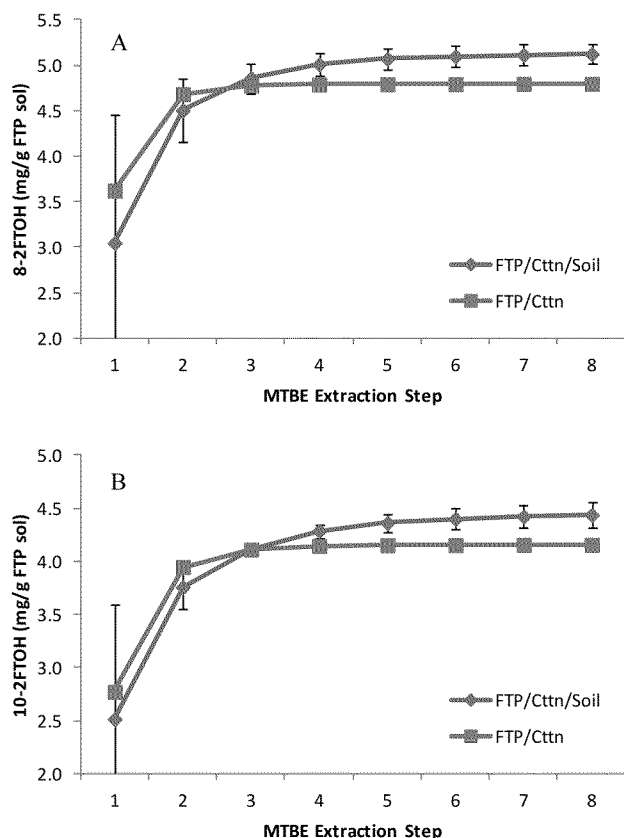

Figure 5. Recovery of 8-2FTOH (a) and 10-2FTOH (b) vs extraction step for FTP4 dried on cotton (n = 3). Extraction was performed with MTBE on the FTP by itself as well as in the presence of 5 g of soil. Note that (i) in all cases little to no additional analyte was recovered after four extraction steps, both with and without the presence of soil in the extraction vessel; and (ii) cumulative error bars (1 SD) diminish after the first two extractions reflecting the effect of serial extractions on assuring all replicates are effectively extracted. Error for FTP/cotton is not shown for clarity, but is similar to FTP/cotton/soil steps 3–8.

8-2FTOH and 10-2FTOH, recovery accumulated through the first four extraction steps after which little to no additional FTOHs were recovered.

Exhausting PFASs through Serial Extractions. Assessment of efficacy for extracting PFASs from FTPs during FTP-degradation experiments must account for an expected dramatic increase in these compounds during the course of the experiment. In fresh FTP sols, concentrations of PFASs generally are relatively low, on the order of 0.1% to 1% of the uncharged fluorotelomer monomers which are intentionally present in the sols, acting as surfactants to stabilize the FTPs in suspension. During FTP degradation experiments, large fractions of the uncharged fluorotelomer monomers, and at least some FTPs themselves, can degrade to bolster PFASs substantially.[10] Given these dramatic changes, methods that are

effective in exhausting fresh FTPs of low PFAS levels are not necessarily effective at exhausting higher concentrations that can be expected following FTP aging. To account for this effect during method development, we spiked our FTP sol with roughly 2 times the levels we observed at the end of our first degradation experiment[10] on a mole-per-g-FTP basis with PFOA (C8 = 125 µg/g FTP), PFDA (C10 = 145 µg/g FTP), and PFDoDA (C12 = 179 µg/g FTP). Then we heat-cured an aliquot of the FTP on cotton tufts, following methodology we established as described above.

Whereas uncharged fluorotelomer monomers have been shown to dissolve in MTBE effectively,[10,26] PFASs tend to dissociate to anionic species, and these compounds generally are more effectively extracted from environmental media with $ACN-H_2O$ solutions.[10] Extraction of impurities and degradation products from FTPs, however, is complicated because the surface tension of FTPs with $ACN-H_2O$ solutions generally exceeds that sufficient to allow wetting of the FTP, thereby minimizing the FTP–solution interface, potentially rendering FTP-sorbed fluorinated compounds shielded from dissolution. Given these concerns, we investigated first targeting extraction of uncharged fluorotelomer monomers with MTBE according to our summary above, of which known fractions of the MTBE were dedicated to analysis of fluorotelomer monomers on GC/MS and PFASs on LC/MS/MS. We then continued extraction of the FTP with $ACN-H_2O$ after MTBE had dispersed the FTP and other fluorinated compounds, specifically targeting perfluorinated anions for analysis on LC/MS/MS. Following the general procedure we used in the past with numerous sample matrices, we investigated extracting the spiked PFASs from the FTP and FTP–soil microcosms using serial extraction steps with 60/40 ACN/H_2O, followed by MTBE liquid–liquid cleanup of the extracts.[3,23] For these efforts, we found acceptable recoveries when extracting from the FTP alone for all spiked PFCAs (C8, C10, C12), as we did with the FTP–soil microcosm, for C8. However, recoveries from the FTP–soil microcosms remained poor for C10 (~ 60%) and C12 (~ 50%) following six extraction steps. Following six serial 60/40 ACN/H_2O extraction steps, we tried extracting these FTP–soil microcosms with solvents having at least moderate miscibility with water (so as to avoid dehydrating soil organic matter)[26] and having low and high dipole moments, butanol and propylene carbonate, respectively, yet C10 and C12 recoveries still remained low.

Given the observation that C10 and C12 were well recovered without soil present but poorly recovered with soil present, we reasoned that perhaps natural organic matter (NOM) in the soil scavenged fractions of the C10 and C12. Following this logic, we investigated preoxidizing NOM in the FTP–soil microcosms with potassium permanganate ($KMnO_4$) and H_2SO_4 to dissolve the NOM, thereby releasing NOM-bound C10 and C12; this effort yielded substantially higher levels of C10 and C12 (data not shown). To investigate whether the higher recoveries of this aggressive preoxidation step might degrade the FTP, we performed the extraction, with and without $KMnO_4/H_2SO_4$ preoxidation, on the 8-2 fluorotelomer acrylate (8-2FTAc) monomer in soil microcosms. Degradation of FTAc proceeds by ester hydrolysis to form the fluorotelomer alcohol (FTOH). Comparing FTOH levels, preoxidized microcosms had up to 12 times higher concentrations than concentrations of nonoxidized controls, suggesting that oxidation potentially could destroy the FTP bonds, so this pre-extraction treatment was rejected.
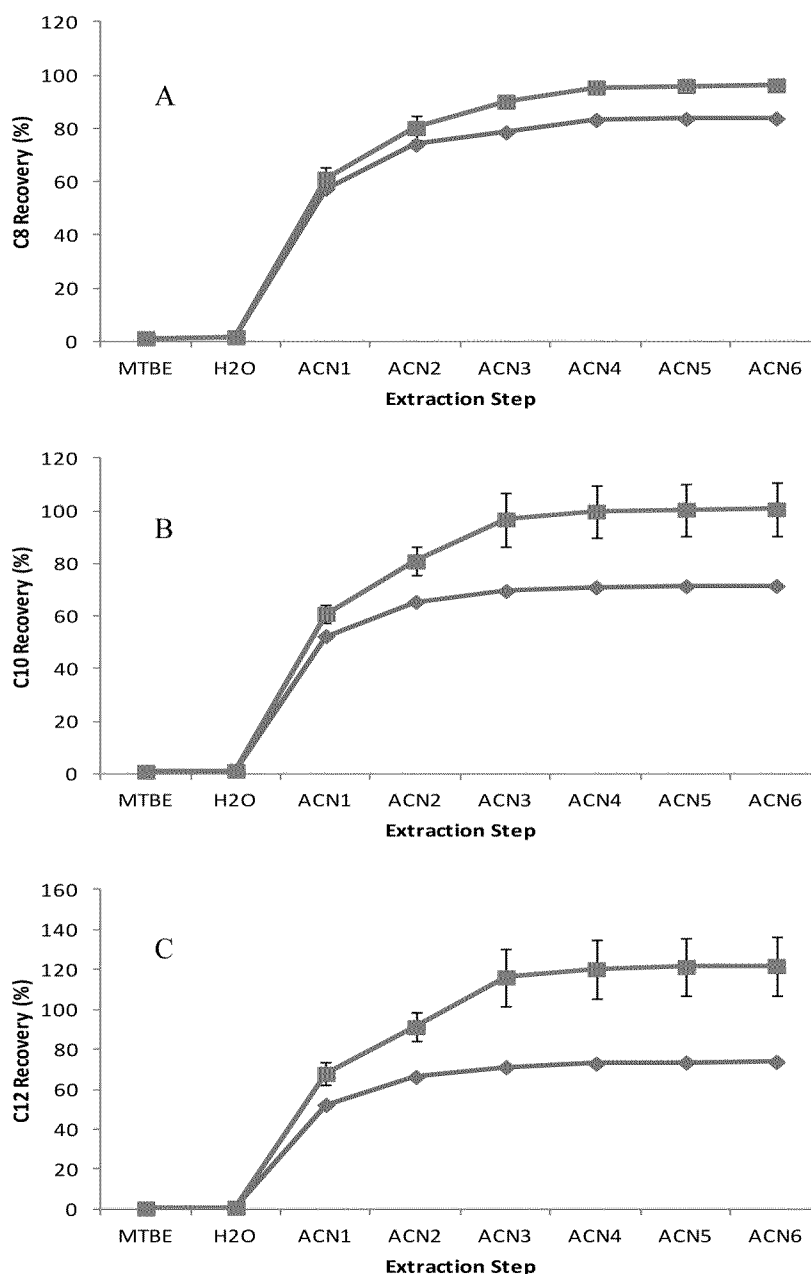
Figure 6. Recovery of C8 (a), C10 (b), and C12 (c). Extracting for FTOHs with MTBE/H_2O followed by 90/10 ACN/H_2O, with two ion-pairing cleanups (cleanup 1 is blue, 2 is red) of each extraction step successfully recovered most of the spiked analytes with four ACN extraction steps. C10 and C12 are reported here from external calibrations. Error bars are cumulative 1 SD (n = 3 microcosms) for the second ion-pairing cleanup.

Investigating the chromatographic retention factor for perfluorocarboxylates on a fluorotelomer stationary phase over a range of ACN/H_2O ratios, Marchetti et al.[27] found a retention minimum at 90/10 ACN/H_2O. Following this lead, we investigated serial extractions of the FTP and FTP–soil microcosms with 90/10 ACN/H_2O, finding considerably improved efficacy for exhausting C10 and C12 from the FTP–soil microcosms (Figure 6). Reasoning that we might be losing part of the recovered analytes to MTBE saturation during our extract cleanup step, in concert with this effort, we investigated performing multiple cleanups of our extracts and found we achieved roughly 100% recovery of all our spiked PFCAs by performing four serial 90/10 ACN/H_2O extractions, with two serial MTBE cleanups of each extract (Figure 6).

Sonication vs Rotisserie for Extracting FTSs and PFASs. Extraction efforts described to this point for FTSs and PFASs entailed 16-h overnight rotisserie mixing. Having established extraction solvents and number of serial steps, we compared the 16-h rotisserie mixing with 1-h sonication performed in crushed ice in 15-m intervals, separated by 15 s of vortexing. For FTOH extraction, rotisserie and sonication were comparable for 8-2FTOH, but sonication yielded substantially higher levels of 10-2 and 12-2FTOH, both for the FTP by itself and for FTP–soil microcosms (Figure 7). In contrast, extraction of PFASs was less effective with sonication than rotisserie, with 4-round sonication recovery at roughly 50% and less for C8, C10, and C12 (data not shown), compared to roughly 100% recovery with rotisserie (Figure 6).
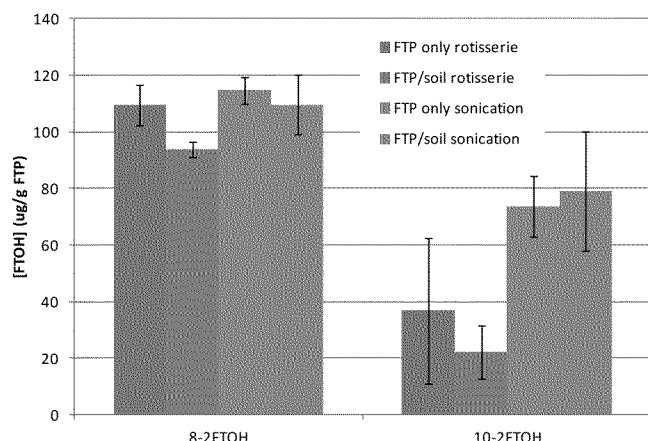
Figure 7. Recovery of FTOHs from an FTP by 4 serial extractions with MTBE/H$_2$O carried out by 16-h rotisserie vs 1-h sonication on ice. Three replicates per treatment, mean ±1 standard deviation. Whereas the extraction methods are comparably efficacious for 8-2FTOH, sonication recovers substantially higher levels of 10-2FTOH.

RESULTS AND DISCUSSION

On the basis of all the methods development we reported herein, the overarching extraction procedure that we found effective for characterizing residuals, impurities, and degradation products in heat-dried FTPs is summarized as Figure 8. This methodology yields reproducible results for new and aged FTPs, whether alone in the extraction vessel or in a soil matrix for degradation experiments. The equations to express analytical concentrations on a per-mass-FTP basis (Step 4 in Figure 8) are given as SI eqs S4−S6. On the basis of the present work, as well as our previous effort,[10] this general approach should be compatible with testing of other FTPs. However, no single procedure can be assured a priori of yielding an exhaustive report of residuals, impurities, and degradation products. Consequently, testing of each step for each FTP is advisable considering the heterogeneous and complex chemical nature of these materials.

The sequence for the overarching methodology that we recommend in Figure 8 is dictated by the fact that FTP residuals, impurities, and degradation products fall into two general camps with regard to molecular structure, extraction-solvent compatibility, and analytical methodology. Uncharged fluorotelomer monomers, e.g., FTAcs and FTOHs, tend to dissolve well in MTBE and typically are analyzed by GC/MS, assuming no complications imparted by the FTP matrix. By extracting FTP samples with serial aliquots of MTBE, four aliquots for the FTP4 we tested here, we were able to exhaust the FTP of these compounds, as judged by diminished recoveries in subsequent MTBE aliquots. Charged PFASs, e.g., fluorotelomer acids and perfluorocarboxylates, dissolve sparingly in MTBE, but the MTBE extraction does foster dispersion of PFASs from the FTP phase, thereby enhancing PFAS recovery.[10] Following extraction of the FTP with MTBE, we were able to exhaust the FTP of these charged analytes with four serial extractions of 90/10 ACN/H$_2$O, as judged by spike and recovery. As a final cautionary note, thermodynamic modeling of data from Marchetti et al.[27] suggests that even 90/10 ACN/H$_2$O may be only marginally effective in extracting, from FTPs, PFASs that are C14 and longer if present (SI Discussion S3).

ASSOCIATED CONTENT

* Supporting Information
Additional discussion, figures, and tables as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org/.
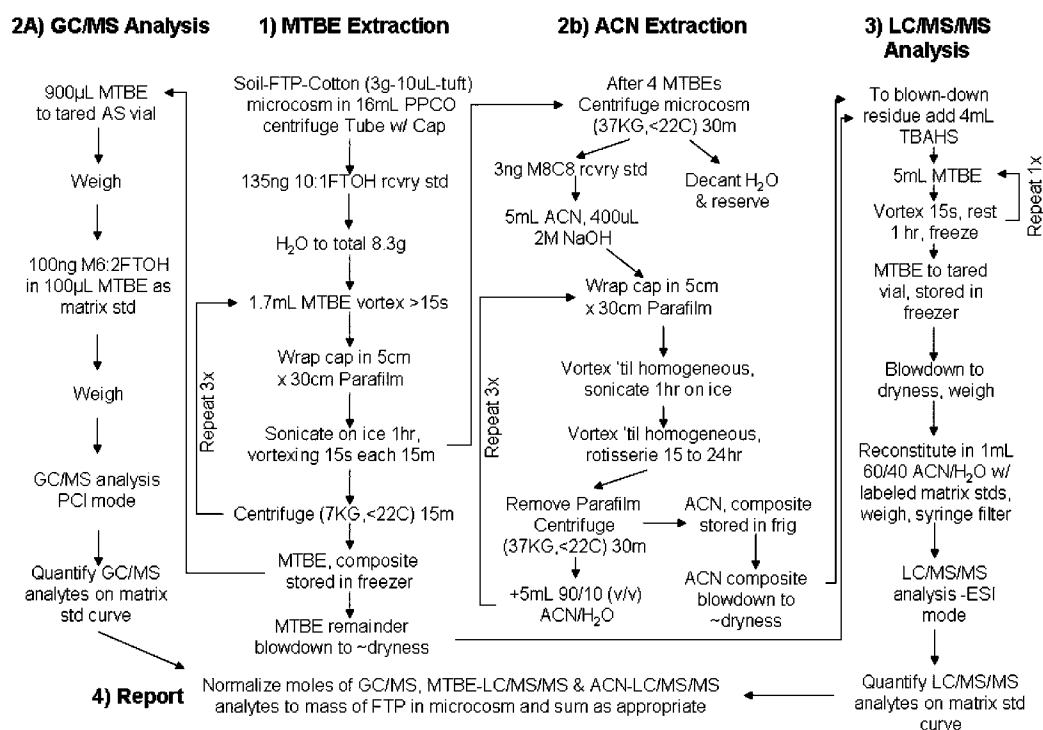

Figure 8. Flow diagram for exhaustive extraction of fluorotelomer monomers and PFASs from a FTP or FTP−soil microcosm. TBAHS is a 0.25 M tetrabutylammonium hydrogen sulfate solution.[23]

AUTHOR INFORMATION

Corresponding Author
*E-mail: Washington.john@epa.gov; phone: 706 355 8227.

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Butt, C. M.; Mabury, S. A.; Muir, D. C. G.; Braune, B. M. Prevalence of long-chained perfluorinated carboxylates in seabirds from the Canadian arctic between 1975 and 2004. Environ. Sci. Technol. 2007, 41 (10), 3521−3528.

(2) Nakayama, S. F.; Strynar, M. J.; Reiner, J. L.; Delinsky, A. D.; Lindstrom, A. B. Determination of perfluorinated compounds in the Upper Mississippi River basin. Environ. Sci. Technol. 2010, 44 (11), 4103−4109.

(3) Washington, J. W.; Yoo, H.; Ellington, J. J.; Jenkins, T. M.; Libelo, E. L. Concentrations, distribution, and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA. Environ. Sci. Technol. 2010, 44 (22), 8390−8396.

(4) Calafat, A. M.; Wong, L. Y.; Kuklenyik, Z.; Reidy, J. A.; Needham, L. L. Polyfluoroalkyl chemicals in the US population: Data from the National Health and Nutrition Examination Survey (NHANES) 2003−2004 and comparisons with NHANES 1999−2000. Environ. Health Perspect. 2007, 115 (11), 1596−1602.

(5) C8SciencePanel. C8 Probable Link Reports. http://www.c8sciencepanel.org/.

(6) Kannan, K.; Perrotta, E.; Thomas, N. J. Association between perfluorinated compounds and pathological conditions in southern sea otters. Environ. Sci. Technol. 2006, 40 (16), 4943−4948.

(7) Naile, J. E.; Wiseman, S.; Bachtold, K.; Jones, P. D.; Giesy, J. P. Transcriptional effects of perfluorinated compounds in rat hepatoma cells. Chemosphere 2012, 86 (3), 270−277.

(8) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. Environ. Sci. Technol. 2006, 40 (1), 32−44.

(9) Russell, M. H.; Berti, W. R.; Szostek, B.; Wang, N.; Buck, R. C. Evaluation of PFO formation from the biodegradation of a fluorotelomer-based urethane polymer product in aerobic soils. Polym. Degrad. Stab. 2010, 95 (1), 79−85.

(10) Washington, J. W.; Ellington, J. J.; Jenkins, T. M.; Evans, J. J.; Yoo, H.; Hafner, S. C. Degradability of an acrylate-linked, fluorotelomer polymer in soil. Environ. Sci. Technol. 2009, 43 (17), 6617−6623.

(11) Federal Register. Premanufacture Notification Exemption for Polymers; Amendment 75. 17. http://www.gpo.gov/fdsys/pkg/FR-2010-01-27/pdf/2010-1477.pdf.

(12) EPA 2010/2015 PFOA Stewardship Program. http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html.

(13) Ritter, S. K. Fluorochemicals Go Short. CEN Online 2010, 88 (5), 12−17.

(14) Rankin, K.; Mabury, S. A. Influence of fluorination on the characterization of fluorotelomer-based acrylate polymers by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Anal. Chim. Acta 2014, 808, 115−123.

(15) Russell, M. H.; Berti, W. R.; Szostek, B.; Buck, R. C. Investigation of the biodegradation potential of a fluoroacrylate polymer product in aerobic soils. Environ. Sci. Technol. 2008, 42 (3), 800−807.

(16) U.S. EPA. Polymer Exemption Guidance Manual; EPA 744-B-97-001; Office of Pollution Prevention and Toxics: Washington, DC, 1997.

(17) Yoo, H.; Washington, J. W.; Ellington, J. J.; Jenkins, T. M.; Meill, M. P. Concentrations, distribution, and persistence of fluorotelomer alcohols in sludge-applied soils near Decatur, Alabama, USA. Environ. Sci. Technol. 2010, 44, 8397−8402.

(18) Yoo, H.; Washington, J. W.; Jenkins, T. M.; Libelo, E. L. Analysis of perfluorinated chemicals in sludge: Method development and initial results. J. Chromatogr., A 2009, 1216 (45), 7831−7839.

(19) Larsen, B. S.; Stchur, P.; Szostek, B.; Bachmura, S. F.; Rowand, R. C.; Prickett, K. B.; Korzeniowski, S. H.; Buck, R. C. Method development for the determination of residual fluorotelomer raw materials and perflurooctanoate in fluorotelomer-based products by gas chromatography and liquid chromatography mass spectrometry. J. Chromatogr. A 2006, 1110 (1−2), 117−124.

(20) U.S. EPA. USEPA-DuPont Supplemental Environmental Project (SEP) Documents. EPA Public Docket EPA-HQ-OPPT-2011-0991. www.regulations.gov/.

(21) de Voogt, P.; Saez, M. Analytical chemistry of perfluoroalkylated substances. TRAC-Trends Anal. Chem. 2006, 25 (4), 326−342.

(22) Van Leeuwen, S. P. J.; Karrman, A.; Van Bavel, B.; De Boer, J.; Lindstrom, G. Struggle for quality in determination of perfluorinated contaminants in environmental and human samples. Environ. Sci. Technol. 2006, 40 (24), 7854−7860.

(23) Washington, J. W.; Henderson, W. M.; Ellington, J. J.; Jenkins, T. M.; Evans, J. J. Analysis of perfluorinated carboxylic acids in soils II: Optimization of chromatography and extraction. J. Chromatogr. A 2008, 1181 (1−2), 21−32.

(24) Tseng, P. J.; Dinglasan-Panlilio, J.; Mabury, S. A. Degradation of fluorotelomer-based polymers in the environment. In ICCE 2009 - 12th EuCheMS International Conference on Chemistry and the Environment, Stockholm, Sweden, 14-17 June, 2009; 2009.

(25) Fitzgerald, J. J. Oil, Water and Solvent Resistant Paper by Treatment with Fluorochemical CoPolymers. U.S. Patent US5674961. 1997.

(26) Ellington, J. J.; Washington, J. W.; Evans, J. J.; Jenkins, T. M.; Hafner, S. C.; Neill, M. P. Analysis of fluorotelomer alcohols in soils: Optimization of extraction and chromatography. J. Chromatogr. A 2009, 1216 (28), 5347−5354.

(27) Marchetti, N.; Caciolli, L.; Lagana, A.; Gasparrini, F.; Pasti, L.; Dondi, F.; Cavazzini, A. Fluorous affinity chromatography for enrichment and determination of perfluoroalkyl substances. Anal. Chem. 2012, 84 (16), 7138−7145.